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Solubilization of particles in sediment traps: revising the stoichiometry of mixed layer export

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Abstract. Sinking particles, once caught in sediment trap jars, release dissolved elements into the surrounding medium through leaching from their pore fluids, chemical dissolution and the activity of free exoenzymes. This results in an increase in dissolved elements in the trap jar supernatant. Elemental fluxes as traditionally measured by sediment traps underestimate total export when this particle-associated dissolved flux is not considered. The errors introduced are variable and alter both the absolute levels of flux as well as the stoichiometry of export. These errors have been quantified and corrections applied for samples from sediment traps in the North Atlantic based on measurements of excess dissolved carbon, nitrogen, phosphorus, silica and calcium in the supernatant of the collection cups. At the base of the winter mixed layer, on average $90 \pm 6\%$ of phosphorus fluxes are found as excess phosphate whereas for carbon and nitrogen dissolved concentrations account for $30 (\pm 8)\%$ and $47 (\pm 11)\%$ of total fluxes respectively. Excess dissolved silica is on average $61 (\pm 17)\%$ of total biogenic silica flux. Little ($< 10\%$) of calcium is solubilized. The proportion of dissolved to total flux decreases with trap deployment depth. Calculations of the C:N:P ratios for particles only are well above the Redfield ratios of 106:16:1 (Redfield et al., 1963), although the mid-water dissolved N:P and N:Si values as well as the C:N:P ratios of remineralisation along isopycnals conform to the Redfield ratios at this site. Accounting for dissolved fluxes of all these elements brings the stoichiometry of export in agreement with the Redfield Ratio and with other geochemical estimates of winter mixed layer export. A factor of 3 to 4 higher ratios of organic: inorganic carbon export also implies that the net atmospheric CO_2 sequestration by the biological pump is about 50% higher at this site when the dissolved elemental fluxes are considered. Solubilization is thus a process that should be accounted for in protocols used to measure vertical fluxes with sediment traps.

1 Introduction

The biogenic production of particles in the surface ocean leads to incorporation of major and minor elements into organic material or on matrices that, after coagulation and aggregation sink out of the upper mixed layer and transport these elements to the deep sea and sea floor. The proportion in which these elements leave the surface mixed layer determines their relative residence times at the surface and their deep-water stoichiometry. Since Redfield et al. (1963) pointed out the relative constancy of the ratios of carbon, nitrogen and phosphorus (C, N and P) in organic matter and dissolved inorganic N:P in the deep sea, this concept has been widely used to estimate fluxes of one element based on those of the others (e.g. MacCreedy and Quay, 2001). Indeed, this ratio is so accepted as being the “norm” that deviations in the so-called “Redfield ratios” of particles in surface waters are interpreted as “overproduction” of carbon, or an elevated efficiency of the biological pump (Körtzinger et al., 2001a; Engel et al., 2002). In the mesopelagial, changes in these ratios in sinking particles with depth are taken to reflect the remineralisation time and length scales of different elements (Honjo et al., 1982; Honjo and Manganini, 1993). Among the other bio-active elements, silicon (specifically the N:Si ratio in upwelled water) determines the contribution of diatoms to new production, thus influencing species succession in a way that is important for particle export. Additionally, the ratio of inorganic carbon (primarily calcium carbonate) to organic carbon in particles exported from the winter mixed layer determines the efficiency of net atmospheric CO_2 sequestration (Antia et al., 2001). Both silica and carbonates are thought to play a prominent role in ballasting material to accelerate its sinking speed (Armstrong et al., 2002; Klaas and Archer, 2002), so their contribution to sedimenting particles can potentially alter the efficiency of bulk export. For all these reasons, being able to accurately determine the fluxes of different elements and their ratios to each other is important in studies of ocean biogeochemistry.

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Sediment traps, more correctly called particle interceptor traps, have been used for several decades to quantify and characterize the flux of elements from the surface to the deep sea. Despite uncertainties in the efficiency with which traps collect the true settling flux, they are still the sole means by which time-series sampling of sinking particles is done in the mid-ocean. Valuable insights into the close coupling of surface processes with mesopelagic and benthic fluxes as well as novel information on the vertical fluxes of major and minor elements has emerged from trap studies, contributing to our understanding of ocean biogeochemical cycles. Almost simultaneous with the enthusiasm in deploying traps in numerous environments came the sobering realization that they fell short of collecting the “true” sinking flux (e.g. Gardner, 1980, 2000; Buesseler, 1991; Gust et al., 1992, 1996). Of the many issues addressed, hydrodynamic biases (resulting from current speeds, trap tilt and trap geometry) appear to be a major problem, causing under- or over-collection of particles and sorting of particles based on size or other properties (Gust et al., 1996). In practice, though, the general acceptance was that once particles were caught, they could be well measured using conventional protocols for particulate analyses. Although the possible errors due to particle solubilization were pointed out early on (for example by the US GOFS Working Group on Sediment Trap Technology and Sampling; Knauer and Asper, 1989), this practice has persisted, largely due to a paucity of information quantifying the potential problem, and the differing deployment configurations and sites where traps are used.

A number of studies have reported solubilization/degradation of organic carbon (Gardner et al., 1983; Noji et al., 1999; Honjo et al., 1995), and nitrogen (Hansell and Newton, 1994; Kähler and Bauerfeind, 2001) amino acids (Lee and Cronin, 1984; Lee et al., 1992), fatty acids (Körtzinger et al., 1994), phosphate (Knauer et al., 1984; von Bodungen et al., 1991), dissolved inorganic nitrogen (primarily ammonium, Knauer et al., 1990; von Bodungen et al., 1991), silica (von Bodungen et al., 1991; Bauerfeind et al., 1997; Antia et al., 1999), metals (Knauer et al., 1984; Pohl et al., 2004) and particulate barium (Dymond and Collier, 1996). Despite finding that solubilization can account for a substantial proportion of the measured particulate flux, to date there has been no systematic analysis of the corrections that may need to be applied to arrive at values of the entire flux arriving in the trap. As important as errors in the absolute levels of flux are changes in the ratios of the elements to each other, as mentioned above.

When compiling existing data from the literature on dissolved compounds in trap supernatant, it became apparent that while some studies had looked at individual compounds no comprehensive data existed in which the major elements were measured for a single set of samples. The aim of this study is thus to measure the degree of solubilization of major elements (carbon, nitrogen, phosphorus, silica and calcium) from particles captured by sediment traps at different depths

from long-term moorings in the North Atlantic and assess how this process affects the measurement of the stoichiometry of export.

2 Materials and methods

Conical, 0.5 m² aperture Kiel-type sediment traps were deployed on 3 moorings at the European continental margin at depths between 600 m and 4000 m. Details of mooring deployment and sample processing are given in Antia et al. (1999). Sedimentation rates of particulate organic carbon and nitrogen (POC and PON) and particulate biogenic silica (PSi) presented here are available from the OMEX database (<http://www.bodc.ac.uk/projects/omex.html>). Particulate organic phosphorus (POP) was measured after filtration, oxidation and colorimetric determination after Grasshoff et al. (1999).

Seawater from ca. 1000 m depth at the mooring sites, with borax-buffered mercuric chloride (final concentration 0.14%) added as a poison, was used to fill the trap jars prior to deployment. Dissolved carbon, nitrogen, phosphorus and silicate were measured in this water and these values were used as background concentrations. After recovery and transport to the laboratory, sample cups were placed upright and particles allowed to settle to the bottom of the cups before further analyses. Supernatant water from above the particle pellet was carefully pipetted out, filtered through sterile 0.45 µm polycarbonate filters and stored at 4°C in the dark. Samples were processed in the order in which they were exposed in the traps so that, including time of deployment and time between recovery and processing, all samples had been in the poisoned jars for at least 5 months and up to 1 year before analysis.

The supernatant was analyzed for the following variables: nitrate, nitrite, ammonium, silicate and phosphate, dissolved organic carbon (DOC) and nitrogen (DON) and dissolved calcium. NO₂, NO₃, NH₄, PO₄, SiO₄ were analyzed using the manual methods described in Grasshoff et al. (1999). Samples were diluted 1:10 before nitrate analyses to keep the level of mercuric chloride below 0.02%, so as not to compromise the efficiency of the cadmium reductor. DOC and DON were analyzed using the high temperature catalytic oxidation (HTCO) method and dissolved calcium using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP AES) analyses. Dissolved organic phosphorus was measured in 119 samples as the increase in phosphate concentration after treatment with a strong oxidizing agent (Oxisolv, Merck).

The excess dissolved concentration of each element in supernatant was calculated as the difference between the measured value and the background value in water used to fill the sample cups. Total fluxes were calculated from the sum of dissolved and particulate fluxes of each element. In several cases and in particular for phosphorus, mean fluxes showed large variations due to extreme outliers in the data. These

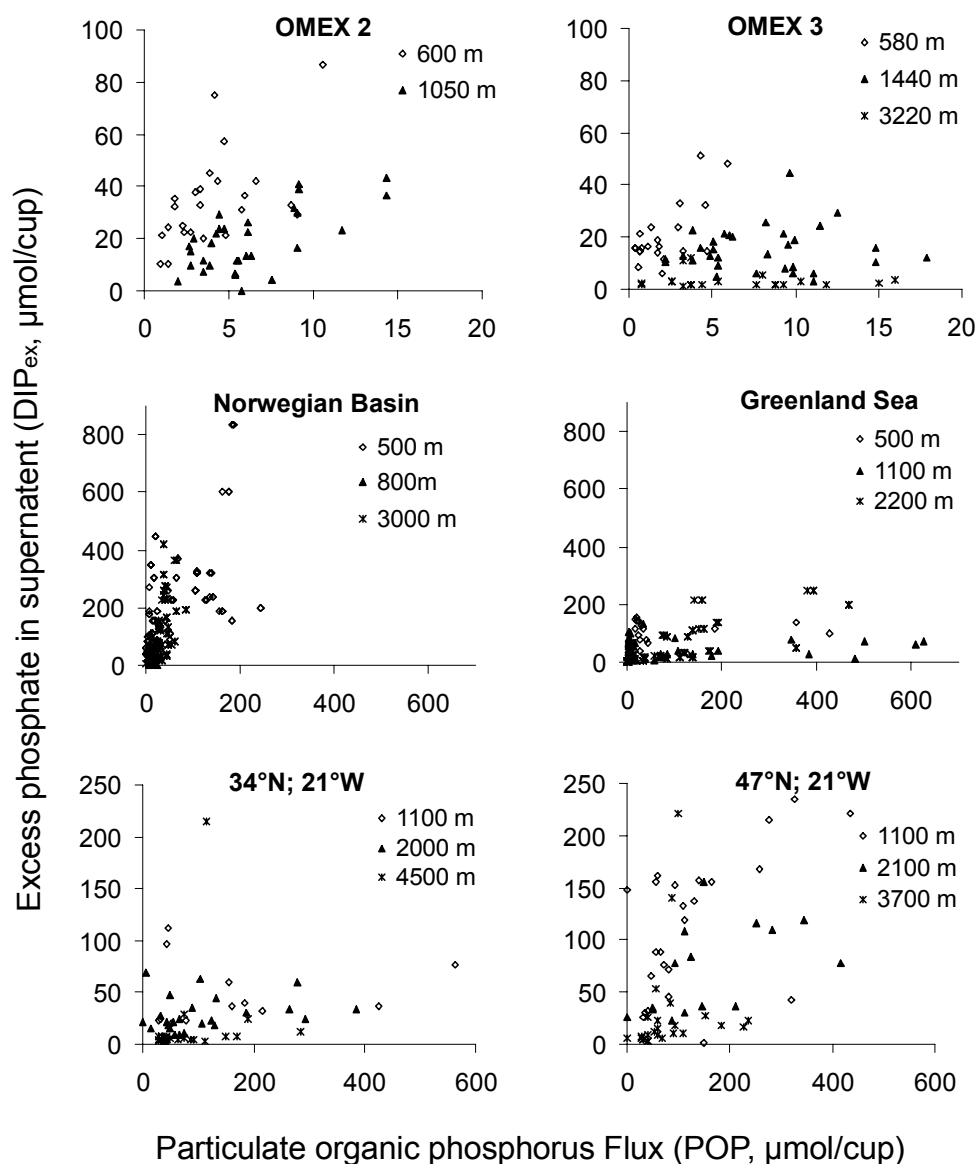


Fig. 1. Relationship between particulate organic phosphorus (POP) and excess dissolved phosphate (DIP_{ex}) in sediment trap cups at different sites and depths as listed in Table 1.

were defined as values lying outside of three standard deviations from the mean and discarded from calculations. Generally 0, 1 or 2 outliers per set of 21–40 values were identified and eliminated.

Measurements done on the OMEX traps are compared to literature values taken from trap deployments in other environments. Data from the Greenland and Norwegian Seas were provided by the Special Research Project (313) of the University of Kiel and are available under <http://www.ifm.uni-kiel.de/jgofs/dm/>. Data from traps in the Southern Ocean are reported in Trull et al. (2001) and were obtained from Bray et al. (2000). The sources of other data are given in the caption of Table 1.

3 Results

3.1 Excess phosphorus in supernatant

For all elements examined, moderate to substantial excess dissolved concentrations in supernatant were found. This was most pronounced for phosphorus, with a mean of $90 \pm 6.4\%$ of the total phosphorus in trap jars found as excess phosphate (DIP_{ex}) in supernatant at 600 m at the OMEX 3 site (Fig. 1a, Table 1). Excess dissolved organic phosphorus could not be detected, with a mean measured concentration of $1.04 \pm 2.7 \mu\text{M}$. With increasing trap depth the proportion of DIP_{ex} to total phosphorus found in the cups

Table 1. The percentage contribution of excess dissolved organic carbon (DOC_{ex}), dissolved organic- and inorganic nitrogen (DON_{ex} , DIN_{ex}), dissolved inorganic phosphorus (DIP_{ex}), dissolved calcium (DCa_{ex}) and silicic acid (DSi_{ex}) to total (particulate + dissolved) carbon, nitrogen, phosphorus, calcium and silica fluxes (TC, TN, TP, TCa and TSi, respectively) in sediment traps below the winter mixed layer.

Site	Depth (m)	DOC_{ex} (%TC) Mean \pm SD	DON_{ex} (%TN) Mean \pm SD	DIN_{ex} (%TN) Mean \pm SD	DIP_{ex} (%TP) Mean \pm SD	DCa_{ex} (%TCa) Mean \pm SD	DSi_{ex} (%TSi) Mean \pm SD	Brine	Poison
European Continental Margin ¹	600	29.9 \pm 6.6	44.5 \pm 10.5	2.8 \pm 2.5	85.8 \pm 18.6	7.7 \pm 4.9	42.9 \pm 20.0	no	HgCl ₂
“	1100	28.3 \pm 9.0	44.4 \pm 10.8	3.9 \pm 1.1	70.6 \pm 18.3	7.5 \pm 5.3	33.2 \pm 11.6	no	HgCl ₂
“	600	28.2 \pm 8.2	45.4 \pm 45.4	1.7 \pm 1.0	90.4 \pm 6.4	7.5 \pm 5.0	60.9 \pm 7.4	no	HgCl ₂
“	1440	17.2 \pm 9.2	29.4 \pm 9.8	5.4 \pm 1.6	61.6 \pm 20.4	9.9 \pm 3.4	35.9 \pm 16.5	no	HgCl ₂
“	3200	9.3 \pm 6.8	12.0 \pm 7.3	4.5 \pm 2.6	34.4 \pm 22.7	8.0 \pm 5.4	21.9 \pm 10.4	no	HgCl ₂
“	4000	7.1 \pm 3.6	16.7 \pm 2.9	1.5 \pm 0.4	15.5 \pm 3.4	3.9 \pm 2.1	6.7 \pm 2.4	no	HgCl ₂
46.45° S; 142.4° E ²	1000						24.5 \pm 10.1	yes	HgCl ₂
“	2000						18.6 \pm 7.6	yes	HgCl ₂
“	3800						23.8 \pm 9.4	yes	HgCl ₂
51.0° S; 141.44° E ²	3300						9.9 \pm 5.5	yes	HgCl ₂
53.44° S; 141.45° E ²	800						4.9 \pm 2.3	yes	HgCl ₂
“	1500						8.3 \pm 3.7	yes	HgCl ₂
34° N; 21° W ³	1071/1248				33.2 \pm 21.5		19.8 \pm 13.5	no	Formalin
“	2067/1894				26.1 \pm 18.9		9.8 \pm 5.4	no	Formalin
“	4564/4391				10.1 \pm 6.1		6.7 \pm 3.0	no	Formalin
48° N; 21° W ³	1081/1202				51.1 \pm 15.1		10.2 \pm 4.4	no	Formalin
“	2018/2200				31.8 \pm 12.5		7.7 \pm 4.9	no	Formalin
“	3718/3749				17.3 \pm 10.8		6.1 \pm 2.9	no	Formalin
Norwegian Basin ⁴	500				79.6 \pm 13.6		34.9 \pm 21.1	no	HgCl ₂
“	800				72.5 \pm 19.7		37.9 \pm 21.6	no	HgCl ₂
“	3000				68.6 \pm 18.4		12.3 \pm 6.3	no	HgCl ₂
East Greenland Sea ⁴	500				78.4 \pm 16.5		35.0 \pm 17.7	no	HgCl ₂
“	1000				64.7 \pm 36.1		35.7 \pm 18.7	no	HgCl ₂
“	2200				39.7 \pm 23.0		22.9 \pm 15.0	no	HgCl ₂
“	500							no	HgCl ₂
“	1000							no	HgCl ₂
“	2200							no	HgCl ₂
Equatorial Pacific ⁵	700	56.0						yes	NaN ₃
“	800						18.7	yes	NaN ₃
“	800						21.7	yes	NaN ₃
“	800						21.4	yes	NaN ₃
Equatorial Pacific ⁶	1095				74 \pm 3			n.g.	NaN ₃
“	1895				70 \pm 3			n.g.	NaN ₃
“	3495				50 \pm 13			n.g.	NaN ₃
“	700				70 \pm 8			n.g.	NaN ₃
“	1600				49 \pm 16			n.g.	NaN ₃
“	3000				26 \pm 10			n.g.	NaN ₃
Greenland Basin ⁷	180/275	33						no	HgCl ₂
“	775/900	50						no	HgCl ₂
“	1735/2100	63						no	HgCl ₂
Greenland Sea ⁸	500			7.8–38	94–98		45–55	no	HgCl ₂

¹This study and Antia et al. (1999); ²Data from Bray et al. (2000), reported in Trull et al. (2001); ³Honjo and Mangannini (1993); ⁴Special Research Project (SFB313), University of Kiel, available at <http://www.ifm.uni-kiel.de/jgofs/dm/>. ⁵Dymond and Collier (1989); ⁶Dymond and Collier (1999); ⁷Noji et al. (1999); ⁸von Bodungen et al. (1991) n.g.=not given

decreased substantially, accounting for 61 \pm 20.4%, 34 \pm 23% and 15 \pm 3.4% of total phosphorus at 1440 m, 3220 m and

4000 m respectively. Site-specific differences in dissolved phosphorus fluxes between these traps and literature values

were small (Table 1), with a similar proportion of total phosphorus as DIP_{ex} at two sites in the Norwegian Sea and East Greenland Sea (ca. 80% at 500 m, decreasing to 68 and 40% at 3000 m and 2200 m respectively; von Bodungen et al., 1991). Lower DIP_{ex} concentrations were found in the temperate north Atlantic at 34° N and 48° N along 21° W, decreasing from 30–50% at 1000 m to 17% at 3700 m and 10% at 4500 m. Weak linear correlations between particulate organic phosphorus and DIP_{ex} were found at all sites (Fig. 1).

Since samples were processed a minimum of 5 months after sample retrieval a time-course of increase in dissolved elemental concentrations in supernatant could not be investigated. After the initial analyses in 1994, splits and supernatant were stored at 4°C in the dark and reanalyzed in 2004 for selected variables. During this long-term storage particulate organic phosphorus showed no decrease, indicating that further degradation or leaching did not occur. For particulate organic phosphorus measured in 1994 (POP_{1994}) and the measurements repeated in 2004 (POP_{2004}) the following relationship was found:

$$\text{POP}_{1994} = 0.09 (\pm 0.07) + 1.03 (\pm 0.28) \text{POP}_{2004}; n = 136, r^2 = 0.89.$$

3.2 Excess silicate in supernatant

High excess dissolved silicate (DSi_{ex}) concentrations were found in all traps studied (Fig. 2). Maximum DSi_{ex} values in supernatant of ca. 1000–1200 μM (at which concentration silicate saturates in seawater at ca. 2°C and pH 8, Rickert et al., 2002) were seen, with the initial slope of PSi to DSi_{ex} decreasing with increasing water depth. Maximal losses of SiO_2 to the dissolved phase at the 500 m horizon amounted to between 61 (± 7.4)% at the OMEX 3 site and 35 (± 21.1)% in the Norwegian Sea. Below 3500 m a relatively constant fraction (6.1–6.7%) of the total siliceous flux was found as DSi_{ex} (OMEX 4 at 4000 m; 34° N, 21° W at 4500 m; 47° N, 21° W at 3700 m). Remarkably low dissolution of SiO_2 into supernatant (<5 to 10%) was seen in traps from the Southern Ocean at 51° S and 53° S, up to an order of magnitude lower than the other sites at similar depth.

3.3 Excess nitrogen in supernatant

For nitrogen too substantial excess concentrations in supernatant were seen. Excess dissolved inorganic nitrogen ($\text{DIN}_{\text{ex}} = \text{excess NO}_3 + \text{NH}_4^+$) was low (ranging from 1.5 to 5.4% of total nitrogen, Fig. 3 and Table 1) and consisted almost exclusively of NH_4^+ . Excess dissolved organic nitrogen (DON_{ex}) accounted by far for the bulk of dissolved nitrogen species and amounted to 45 (± 13)% and 16.7 (± 2.9)% of total nitrogen fluxes in the traps at 600 m and 4000 m, respectively (Fig. 4a). DON_{ex} was linearly related to PON fluxes and showed a decreasing trend as proportion of total nitrogen flux with trap depth.

3.4 Excess carbon in supernatant

A similar trend was observed for excess dissolved organic carbon (DOC_{ex}) in supernatant, in that it was linearly related to POC flux and decreased with increasing trap depth (Fig. 4b). Altogether, 30 (± 6.6)% and 7 (± 3.6)% of total carbon was found as DOC_{ex} at 600 m and 4000 m, respectively. Dissolved inorganic carbon (DIC) was not measured since the cup water was buffered, precluding measurements of the carbonate system. However, an attempt is made to judge the extent of the problem by assuming (as a first approximation) that continual respiration after particles settle in the jars would produce dissolved inorganic carbon (DIC) and nitrogen (DIN) whereas enzymatic degradation and leaching from particles would give out dissolved organic carbon (DOC) and nitrogen (DON), roughly in the Redfield C:N ratio of 6.6:1. Thus, multiplying the DIN concentration by 6.6 the amount of DIC produced in the traps would be 55–316 μM , or 2.8–4.3% of particulate organic carbon (POC) flux and 1.7–3.3% of total organic carbon (POC+DOC) flux.

Excess dissolved Ca (DCa_{ex}) was measured to check for inorganic carbon losses from the particles; there was an increase of 3.9–7.9% in supernatant above background dissolved Ca levels (9.9% at 1440 m). As mentioned, in buffered systems alterations in pH, that would indicate changes in the DIC and alkalinity pools due to calcite dissolution and respiration (that have opposing effects on pH), cannot be used. In unbuffered systems however, a rough calculation (made using the “CO2SYS” program of E. Lewis) indicates that these could cancel each other, resulting in a small loss of calcite at constant pH values. For example, the dissolution of calcite in the traps studies (on average 3 mg calcium per 400-ml cup) would produce an alkalinity increment of 350 $\mu\text{eq/L}$ and DIC change of 175 μM . At a temperature of 4°C, and initial DIC and Alkalinity values of 2100 and 2300 μM , respectively, this would increase pH by 0.2 units. Back-calculating the amount of respiration that would be needed “balance” this (i.e. bring pH back to the original value) yields 111 μM DIC added due to respiration. This is within the range (55–316 μM DIC) estimated to result from respiration in the cups (see previous paragraph). Nonetheless, these processes would have a small effect on total solubilization losses since most organic carbon is lost as DOC with the calcite losses being relatively small. This approach may be useful in shallow, short-term trap deployments where additional measurements of oxygen depletion could be used to constrain the extent of respiration in the jars.

3.5 Swimmer-related excess dissolved fluxes

For the trap at 600 m, where maximal swimmers were found, there was no correlation between swimmer carbon (a better estimation of swimmer flux than numbers alone) and DOC or DON values ($r^2 = 0.17$, $n = 37$). At this depth, swimmer biomass was low compared to total organic carbon and

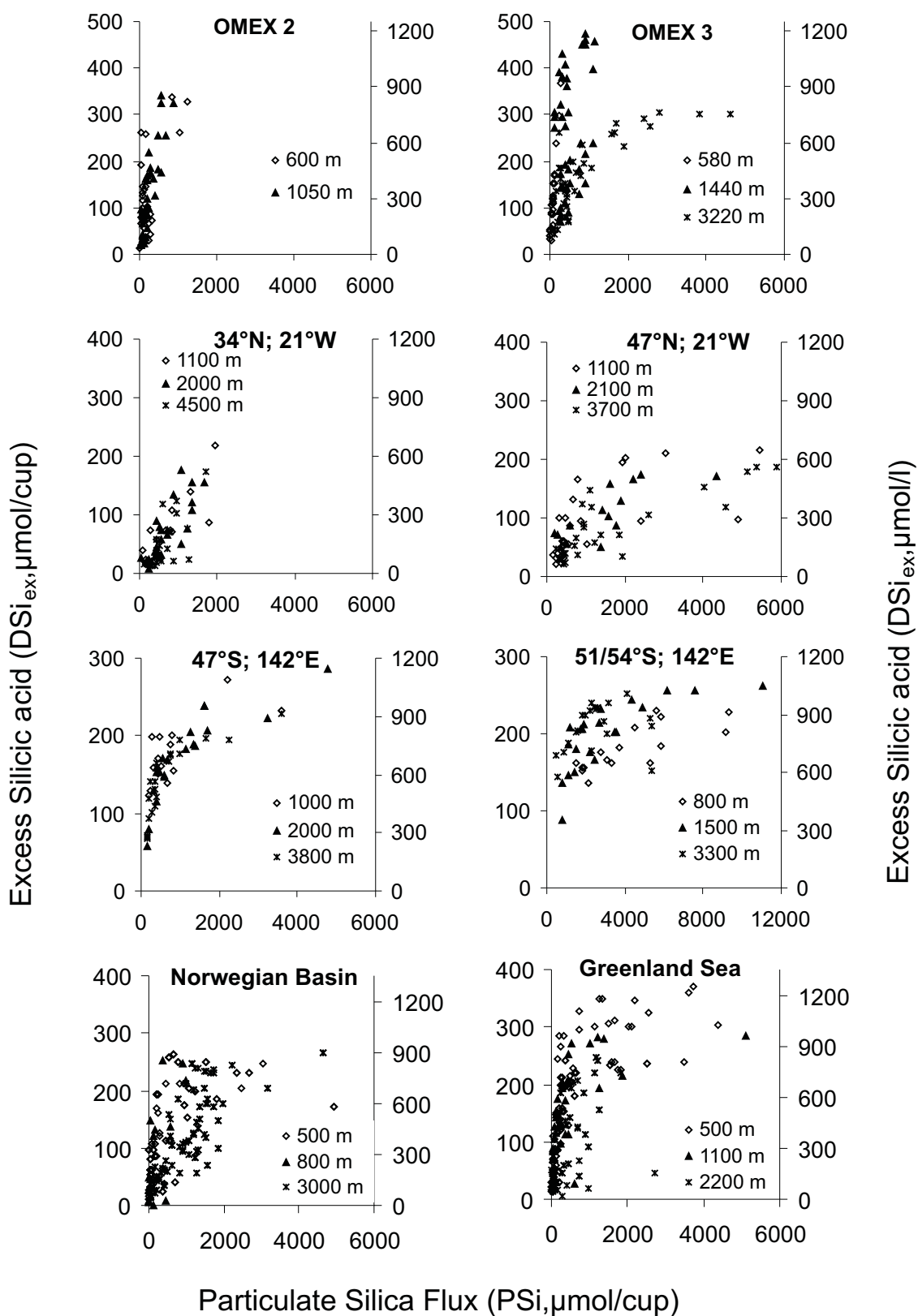


Fig. 2. Relationship between particulate biogenic silica (PSi; x-axes) and excess dissolved silicic acid (DSi_{ex}; left axes) in sediment trap samples at different sites and depths as listed in Table 1. The absolute concentration of silicate in supernatant water is given on the right axes.

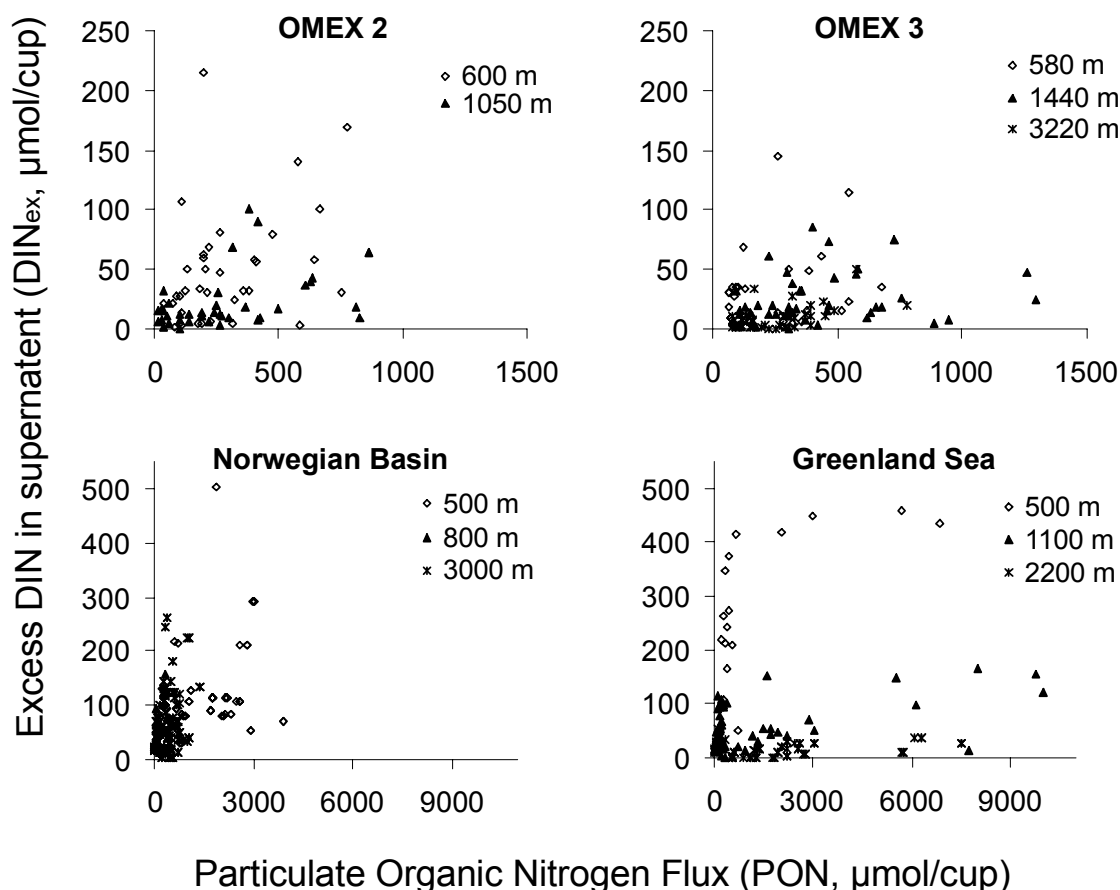


Fig. 3. Relationship between particulate organic nitrogen (PON) and excess dissolved inorganic nitrogen (ammonium and nitrate) (DIN_{ex}) in sediment trap cups at different sites and depths as listed in Table 1.

nitrogen fluxes, accounting for a mean of $10.9 (\pm 7.1)\%$ of total carbon (DOC+POC) in the traps. Even assuming that 20% of the swimmer biomass leached into the surrounding seawater, this effect would be negligible on DOC increase. The contribution of swimmers has therefore been neglected and it is assumed that the excess DOC and DON originated only from passively sinking particles.

3.6 Correction of C:N:P, N:Si and POC:PIC ratios

Table 2 summarizes the molar ratios of C:N:P for the traps analyzed in this study as well as other values from the literature. Relying on information from particulate analyses only, the C:P and N:P ratios are highly in excess of the Redfield value of 106:1 and 16:1 respectively, even though the scatter in the data is large. Where corrections for the dissolved fluxes are available for all elements, mean ratios at the base of the mixed layer are in good agreement with the Redfield ratios, increasing with depth to 4000 m. Large shifts in the POC:PIC ratio are seen when accounting for excess dissolved fluxes, increasing from 2:1 to a mean of 7:1 at 600 m. For nitrogen and silica, similar rates of dissolution result in

large corrections of the absolute flux values but the ratio of N:Si remains unchanged (Table 3).

4 Discussion

The presence of excess dissolved material in the trap supernatant water is the most direct evidence that particles settled within the cups are altered and solubilized during storage. No matter how these excess dissolved concentrations result: from continual particle degradation, passive leaching of aggregate pore fluids, through gradual physical breakdown of dead membranes and organic entities, or through chemical dissolution such as for silica and calcium carbonate, a correct estimation of the flux reaching the traps requires correction for this artifact. Determining the contribution of each of these processes to net solubilization is however important in considering traps deployed in differing environments with different conditions of sample storage, treatment and analyses. The analyses here is restricted to mid-water traps with low swimmer abundances, where long-term deployments and storage of samples allows a straightforward determination of

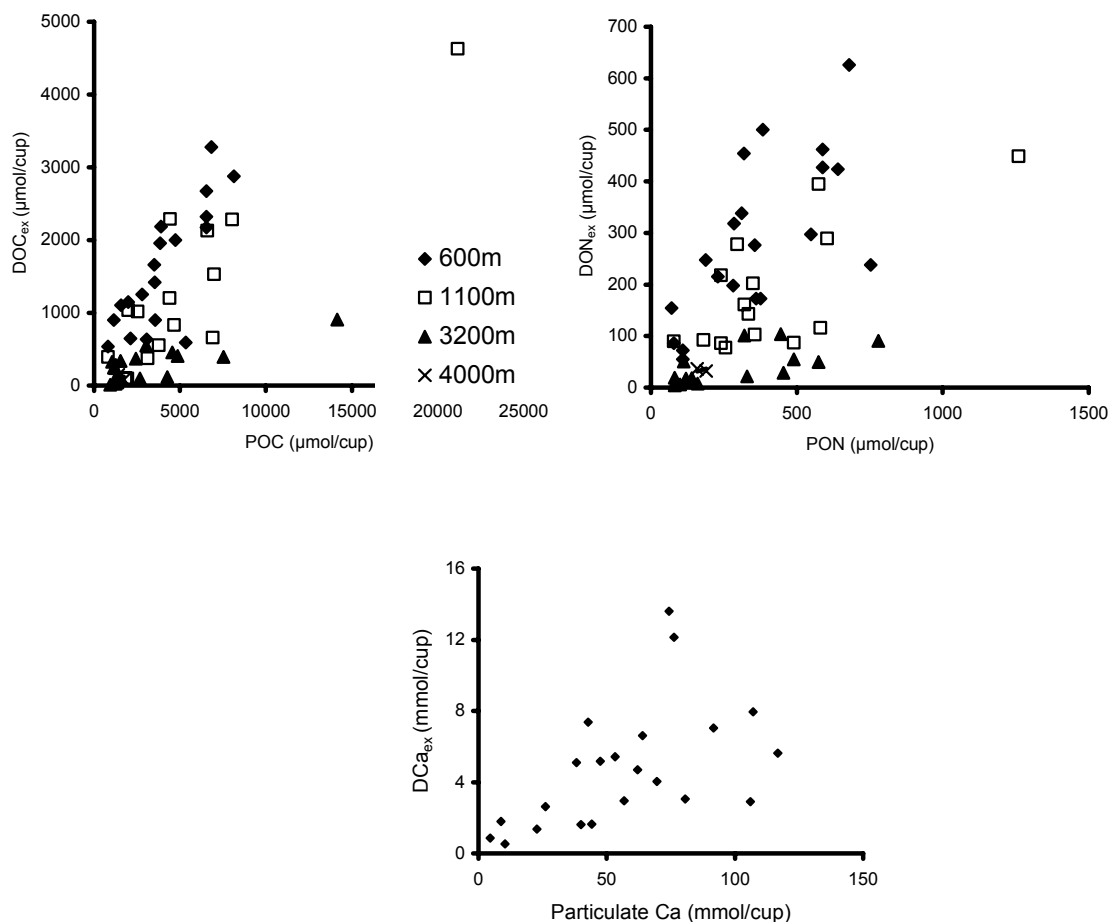


Fig. 4. Relationship between particulate organic carbon (a) and nitrogen (b) to the excess dissolved concentrations of organic carbon and nitrogen respectively. (c) Relationship between particulate calcium and excess dissolved calcium in trap samples. All data are from the OMEX traps only.

excess elements in supernatant. Shallow deployments for merely hours to days in high-swimmer environments would require a different approach, since swimmers are a major source of dissolved elements in such trap samples, and there is no reliable way to separate swimmer contribution of differing elements from that originating from the passive flux.

4.1 Aggregates as “carriers” of dissolved elements

The fact that large sinking aggregates, the main vehicles for vertical elemental fluxes (McCave, 1975; Fowler and Knauer, 1986), carry dissolved loads in their interstitial spaces has been recognized for some time. Aggregates are greatly enriched in DOM and inorganic products of remineralisation and dissolution such as phosphate and silicate (Shanks and Trent, 1979; Alldredge, 2000; Brzezinski et al., 1997; see Simon et al., 2002 for a summary). A substantial fraction of the dissolved loads leave the aggregates within the euphotic zone (Kjørboe et al., 2001). Nonetheless, where the rate of remineralisation by aggregate bacteria exceeds uptake

of substrate and loss through outward diffusion, as found by Smith et al. (1992), pore fluids of aggregates are replenished faster than depleted. Fecal pellets, an important aggregate type, also contain large amounts of dissolved organic matter (DOM) that leach out into the surrounding seawater (Urban-Rich, 1999). Packed with bacteria and heterotrophic protozoa (Silver and Alldredge, 1981; Simon et al., 2002), these micro-environments are hotspots of microbial activity in the water column and greatly affect the cycling of elements in the water column. Investigating the time-course microbial degradation of fresh diatom aggregates, Grossart and Ploug (2001) found significant carbon and nitrogen contents and high microbial turnover rates after 8 days of incubation, during which time aggregates in the natural environment would be well below the winter mixed layer.

As Alldredge (2000) points out, the dissolved loads in the interstitial spaces of aggregates must contribute substantially to vertical flux. However, practically all measurements of DOM within aggregates have been done within the upper

Table 2. Atomic carbon:nitrogen:phosphorus (C:N:P) ratios from the particulate fraction only and total (particulate + dissolved) material in sediment traps and from chemical analyses along isopycnals.

Site	Depth (m)	Ratio in Particles Only				Ratio of Total Flux			
		C:	N:	P	C:N	C:	N:	P	C:N
European Continental Margin ¹	600	724±353	85±30	1	8.3±2.0	104±70	17±7.9	1	5.6±1.6
"	1100	464±291	56±33	1	9.1±2.0	187±110	25±8.4	1	6.5±1.6
"	580	915±426	94±44	1	9.2±2.1	107±69	15±8.0	1	6.1±1.2
"	1440	524±338	52±32	1	9.6±2.9	206±130	30±17.6	1	6.9±1.9
"	3220	317±181	33±16	1	9.7±2.4	236±112	29±12.5	1	7.8±2.1
"	4000	282	26	1	11.3	196	28	1	8.1
Norwegian Basin ²	400	730	49	1	16.3				
"	800	321	25	1	13.1				
"	2950	345	17	1	22.6				
East Greenland Current ³	500	647	59	1	9.6				
"	500	1053	84	1	9.4				
"	500	622	71	1	8.2				
"	1000	331	33	1	8.5				
"	2200	226	30	1	8.9				
"	2310	171	19	1	10.3				
Gulf of Riga ⁴	30	426	49	1	9.3				
Gotland Sea ⁵	140	82	9	1	9.3				
N. Baltic Sea ⁶	40	9 to 13	5 to 22	1					
Sargasso Sea ⁷	150	457	46	1	8.6				
"	150	340	42	1	8.3				
"	300	429	58	1	7.4				
"	300	382	62	1	14.0				
Tasmanian Sea ⁸	300	159	15	1	10.8				
"	1000	129	13	1	9.7				
"	300	193	22	1	8.8				
"	1000	232	22	1	10.5				
48° N ⁹	1000	968	110	1	8.8				
34° N ⁹	1000	430	74	1	5.8				
Sargasso Sea ¹⁰	3694	104	10	1	10.4				
tropical Atlantic ¹⁰	389	182	21	1	8.8				
"	976	274	31	1	8.9				
"	3755	180	18	1	10.3				
"	5068	202	20	1	10.3				
East Hawaii ¹⁰	378			1	9.0				
"	978			1	9.2				
"	2778	303	30	1	10.1				
"	4280	243	10	1	10.4				
"	5582			1	9.2				
Panama Basin ¹⁰	667	318	33	1	9.6				
"	1268	226	26	1	8.8				
"	2700	210	25	1	9.2				
"	3700	243	23	1	10.2				
Estimates from chemical data along isopycnals:									
N. Atlantic ¹¹	200–500					97±9	17.6±0.6	1	5.5
"	500–680					88±6	16.8±0.5	1	5.2
Atlantic, Indian, Pacific Ocean ¹²	500–1000					117±14	16±1	1	
N. Atlantic ¹³	200–500					101±12	14.4±0.7	1	7.2±0.4
"	500–680					131±18	16.8±1.3	1	7.8±0.5

¹This study, ^{2,3}Special Research Project (SFB313), Universität of Kiel, available at <http://www.ifm.uni-kiel.de/jgofs/dm/>. ⁴Reigstad et al. (1999) ⁵Struck et al. (2004). ⁶Heiskanen et al. (1998) ⁷Oceanic Flux Program of WHOI, (<http://www.whoi.edu/science/MCG/ofp/>) ⁸Trull et al. (2001) ¹⁰Honjo and Mangannini (1993) ¹¹Takahashi et al. (1985) ¹²Anderson and Sarmiento (1994) ¹³Körtzinger et al. (2001b)

Table 3. Ratios of particulate organic carbon: particulate inorganic carbon (POC:PIC) and atomic nitrogen: silica (N:Si) ratios from the particulate fraction only and total (particulate + dissolved) material in sediment traps.

Site	Depth (m)	Ratio in particles only		Ratio in total material	
		$C_{org}:C_{inorg}$	N:Si	$C_{org}:C_{inorg}$	N:Si
European Continental Margin	600	2,0±1,2	2,2±1,1	6,1±3,3	2,4±1,3
"	1100	2,1±1,9	1,3±0,9	6,4±3,5	1,3±0,8
"	580	2,1±0,6	3,4±1,9	8,0±1,7	2,5±1,3
"	1440	2,8±2,5	0,9±0,6	4,3±1,7	1,0±0,5
"	3220	1,3±0,8	0,4±0,2	2,6±1,1	0,4±0,2
"	4000	0,8	0,4	1,1	0,4

water column; the DOM load in sub-surface and deep aggregates is unknown. The data presented here provide a first, albeit indirect, estimate of dissolved elemental concentrations in large particles in the mid- and lower water column. Aggregates are thus carriers of significant amounts of dissolved material, here called the “particle-associated dissolved flux”.

The data here can be compared to those of Alldredge (2000) who measured POC and DOC on aggregates from 2–20 m water depth. At these shallow depths DOC was on average 31% of total carbon in the particles whereas in trap material at 600 m depth (this study) DOC_{ex} was on average 30% of total carbon in the cups, suggesting that a significant proportion of labile organic carbon is still being recycled within aggregates reaching the base of the mixed layer, and that losses due to leaching, diffusion and assimilation by organisms on and in the aggregates are lower than the net DOC production rates as shown by Smith et al. (1992). Considerably lower DOC_{ex} , accounting for <10% total carbon, is exported below 1400 m (Fig. 4a). The linear relationship between POC flux and DOC_{ex} implies no significant seasonality in the contribution of dissolved matter to total fluxes, but rather a constant internal aggregate remineralisation by bacteria and protozoa, in proportion to organic matter availability.

4.2 Particle alteration in trap jars

Aside from passive leaching out of large particles, other processes such as continued microbial degradation, the activity of free hydrolytic enzymes, physical destruction of dead organisms and damaged membranes and chemical dissolution could also contribute to the excess concentrations of dissolved elements measured. Particle breakdown by microbial activity is assumed to be stopped by the addition of poison to the cup solution, but this may not be instantaneous. Although at the concentration of mercuric chloride used in this study Lee et al. (1992) reported cessation of microbial activity in a concentrated particle suspension, penetration of the poison into aggregates would be rate-limited by the diffusion coefficient applicable. There is little data on the diffusion constants applicable for aggregates, but these are likely to be considerably slower than for single cells due to the frac-

tal, mucous/gel structure of organic aggregates. Brzezinski et al. (1987) estimated 2 orders of magnitude slower diffusivity rates for silica from diatom aggregates than those for elemental silica through a permeous membrane. This considerably slower transport for solutes into aggregates could result in some continuation of microbial degradation before poison concentrations in the aggregates become effective.

Free enzymes such as phosphatases and proteases are also concentrated in aggregates and though their activity is strongly inhibited by both mercuric chloride and formaldehyde at the concentrations used to poison trap samples (Christian and Karl, 1995; Liu et al., 1997), the same time constraints on penetration of poison as discussed above would apply. In as far as free phosphatases degrade larger dissolved organic entities to phosphate and low molecular weight organic material (Hoppe, 2003), they would contribute to alteration and not production of dissolved species.

For silica and calcium, where dissolution is controlled both by physico-chemical factors as well as biological degradation, dissolution and leaching may continue after microbial activity is stopped. Silica dissolution on organic aggregates is accelerated by destruction of the organic frustule matrix through bacterial protease activity (Bidle and Azam, 2001), and diatomaceous aggregates in the upper water column accumulate silicate in their interstitial spaces at up to 100-fold higher concentrations than in the surrounding seawater (Brzezinski et al., 1997). Although seawater is greatly undersaturated with respect to silicic acid, high siliceous fluxes and leaching out of particles cause saturation of silicate in supernatant water (Fig. 2), presumably stopping further losses. Bauerfeind and von Bodungen¹ show the dissolution kinetics of silicate in sediment traps with a clear saturation at high particulate silica fluxes similar to that recorded here.

During processing of trap samples (picking of swimmers, splitting and filtering), particles are rinsed with seawater and partially broken, and particularly during filtering the interstitial spaces are bled. However, presuming equilibrium between the particles and surrounding seawater during

¹ Bauerfeind, E. and von Bodungen, B.: Loss of biogenic particulate silicon in sediment trap samples through dissolution – does it matter? *Marine Geology*, in review, 2005.

the long storage times used here, adding the excess elemental fluxes in supernatant to the measured particulate flux accounts for this loss. Filtration of particles prior to analysis, whether from water bottles, trap jars or in situ pumps, causes loss of interstitial fluids and underestimation (to some as yet unknown degree) of their elemental loads. This “particle-associated dissolved load” is not measured in either the particulate or dissolved pool using current protocols, and is potentially missing in estimates of elemental standing stocks and vertical flux. This caveat is common to all analyses of particles in the water column and warrants attention in all biogeochemical studies.

4.3 Factors affecting differences in solubilization

Factors such as fixative/poison type, brine, buffer, and presence of swimmers are likely to affect leaching of interstitial fluids. Where data are available (Table 1), traps with similar treatments (e.g. traps in the Greenland Sea, Norwegian Sea and European Continental Margin all had mercuric chloride, with no brine addition), similar proportions of excess dissolved phosphorus and silicate were found in supernatant at similar depths. For silicate, traps in the Southern Ocean showed significantly lower DSi_{ex} concentrations as compared to those from other areas; however, since both the species composition and biogeochemical regimes as well as trap treatment (addition of brine in the Southern Ocean traps) differed, it is difficult to separate these effects. For traps at similar sites and depths (the OMEX traps and data from Honjo and Manganini, 1993), there are factor of 2 differences in the slopes of dissolved to particulate fluxes of phosphorus and silicon measured (Figs. 1 and 2), with higher proportions of dissolved elements in the mercuric-chloride-poisoned OMEX traps. These may be due to differences in poison/fixative used since formaldehyde is known to stabilize membranes and chitinous structures, possibly making them less permeable for leaching (e.g. Lee et al., 1992). Rather unfortunately, the use of formaldehyde as a fixative, as recommended by the JGOFS protocols (http://usjgofs.whoi.edu/protocols_rpt_19.html) precludes DOC/DON measurements in supernatant, the effect of which can be substantial in the mesopelagic zone.

For silica in particular, the initial slope of DSi_{ex} against PSi flux varies both with depth and site. At $51^{\circ}S$ in the Southern Ocean where the large, heavily silicified *Fragillariopsis kerguelensis* dominated diatom export (Trull et al., 2001), the silica dissolution was half of that found at other sites at the same depths. Such site-specific differences in dissolution of biogenic silica has been reported by Rickert et al. (2002) who found a factor of 10 lower dissolution of silica in the Southern Ocean as compared to the Norwegian Sea, related to differences in the reactivity of diatom shells. Species-specific differences in the dissolution of diatom frustules (Kohly, 1998), and strong differences in reactivity of biogenic silica linked to the structural integrity, organic coat-

ing and detrital minerals are manifested in higher silica contents of Southern Ocean sediments as compared to similar latitudes in the North Atlantic (Schlüter et al., 2000).

Although in this study swimmer fluxes were low and negligible compared to the passive sinking fluxes, swimmers may strongly falsify results in shallow traps (Steinberg et al., 1998), where swimmer biomass may equal or exceed the passive sinking flux. Addition of brine, that causes zooplankton swimmers to herniate in the traps (Peterson and Dam, 1990), would magnify the problem. Since swimmers, through herniation, excretion and leaching will introduce large dissolved concentrations that cannot reliably be separated from the fraction originating from sinking particles, swimmer avoidance should be a priority. For very short term deployments of shallow traps solubilization may not present a major problem for all elements, but at present little is known about this problem.

For elements other than those presented here, the rate and degree of dissolution would need to be individually determined. Knauer et al. (1984) showed rapid dissolution of up to >80% and >70% of sedimenting manganese and cadmium respectively and similarly high dissolution, although proceeding at a slower rate, for zinc. Pohl et al. (2004) found only half those values in their traps. Particle-reactive elements such as iron and thorium are, predictably, not found in supernatant (Pohl et al., 2004). These results imply that the application of Th:POC ratios from traps to estimate fluxes based on radionuclide profiles would require an estimate of the relative losses of these elements to the dissolved phase.

Given the differing stoichiometry of POM and DOM and the different time scales of their production and mineralisation (Hopkinson and Vallino, 2005) large aggregates as carriers of both particulate and dissolved material should be treated as a single entity requiring a consolidated analytical approach. This would include collection of interstitial waters during filtration with analyses of excess dissolved elements, as has been done in the upper water column in but relatively few studies (Brzezinski et al., 1997; Alldredge 2000).

4.4 “Correcting” for particle solubilization

Correcting for solubilization losses from particles can have severe to negligible effects depending on element and trap depth, both in terms of the absolute values of flux as well as the stoichiometry of settling material (Tables 2 and 3). Whereas at the base of the winter mixed layer at around 500 m, phosphorus would need to be corrected upwards by a factor of up to 10, carbon and nitrogen flux corrections are between factors of 1.4 to 2. Higher dissolution of silica would bring the total silica fluxes up by a factor of 2 to 2.5. Total calcium fluxes are practically unaffected by solubilization. The “correction factors” are similar to the errors due to hydrodynamic biases of moored traps, estimated by water column radioisotope budgets below the mixed layer (Scholten et al., 2001; Yu et al., 2001). For the OMEX traps,

for example, Scholten et al. (2001) estimate collection efficiencies of ca. 38% at 600 m at both mooring sites, 90% at 1050 m at OMEX 2 and 113% and 128% at 1440 m and 3220 m at OMEX 3. As these authors pointed out, these estimates are to be treated with caution, since no direct measurements in the water column were available at these sites and because of their proximity to the shelf edge, where particularly in the deeper traps lateral advection could have caused the “overtrapping” signal. Nonetheless, it should be pointed out that this correction, based on calculated and measured fluxes of ^{230}Th , is unaffected by solubilization since thorium has a high affinity for particles and is not found in supernatant water (Pohl et al., 2004). The factor of 2.5 “correction” based on the thorium budgets for the 600 m traps is similar in magnitude to that for organic carbon and nitrogen and slightly lower than that for phosphorus when accounting for solubilization. Both these effects (solubilization and hydrodynamic biases) decrease with increasing water depth and, when accounted for, will increase the estimates of mid-water remineralisation rates that have been derived from sediment trap data (e.g. Martin et al., 1987; Antia et al., 2001). These “corrections”, by increasing export estimates, may narrow the gap between measured particle fluxes and those based on subsurface oxygen utilization rates (e.g. Jenkins, 1982). They would also substantially decrease the estimated “lateral” or “advective” fluxes that are assumed where an increase in flux with depth is measured (e.g. Neuer et al., 1997; Antia et al., 1999) and narrow the observed discrepancy between vertical POC fluxes and sediment community carbon demand (Lampitt et al., 1995; Smith et al., 2001). Central to the need or even ability to correct for solubilization, trap collection bias or other artifacts is our confidence in the level of accuracy with which we can measure sinking fluxes and the level of accuracy that is needed for the process to be investigated. With more attention being paid to methodological refinements and calibration of trap behavior under various conditions, a higher level of accuracy can be achieved by applying appropriate protocols for measurement of the collected particles.

4.5 Elemental ratios in total (dissolved + particulate) flux

The ratio of major elements (organic- and inorganic carbon, nitrogen, phosphorus and silicon) leaving the upper mixed layer is crucial in estimating the net sequestration potential of the biological pump and the global distribution of deep-water nutrient ratios. Biogeochemical models routinely use nitrate fluxes to estimate carbon export (e.g. MacCready and Quay, 2001) relying on the mean global validity of the Redfield stoichiometry of C:N uptake in organic matter. Although there is evidence that, at least seasonally, particle formation with a C:N ratio significantly higher than the Redfield Ratio takes place (Körtzinger et al., 2001a; Engel et al., 2002) the present analysis indicates that export at the base of the mixed layer does not reflect this in the annual mean, at least in the North

Atlantic. More such investigations are required from other areas.

A large amount of data on the elemental ratios of sinking particles arising from sediment traps (summarized in Table 2) uniformly shows C:N ratios above the Redfield Ratio at the base of the mixed layer. In a compilation of trap and in situ pump data Schneider et al. (2003) reported particulate C:N ratios above 8.5 below 500 m depth, increasing by 0.2 per 1000 m. The OMEX data reported here are in agreement with this trend for the particulate fraction only. However when corrected for dissolved C, N and P in the traps the elemental ratios are almost exactly 106:16:1 (Table 1). Total C:N ratios not significantly different from the Redfield value (6.1 ± 1.2) at 600 m depth at this site are also in agreement with those calculated by Körtzinger et al. (2001b) along isopycnals at similar depths in the North Atlantic (6.5 ± 0.2). Körtzinger et al. (2001b) in turn revised the previously lower estimate (C:N of $5.1 \pm 0.2:1$) of Takahashi et al. (1985) by subtracting the contribution of anthropogenic CO_2 to total DIC. Total N:P ratios of ca. 16:1 and N:Si ratios of 2.4:1 in sedimenting material at the base of winter mixed layer also agree with long-term means of dissolved nutrients in the mesopelagic zone in the eastern North Atlantic (data from the Levitus Web site <http://ingrid.ldeo.columbia.edu/SOURCES/LEVITUS/>). This shows some consistency in the nutrient stoichiometry of material supply to and remineralization within the subsurface layers, whereas the exceedingly high N:P ratios estimated in the particulate flux fraction only (averaging N:P of 90:1 at 600 m) deviate substantially from the canonical Redfield value.

The depth scales and relative remineralization profiles of carbon, nitrogen and phosphorus as estimated using numerical solutions to large-scale distributions of dissolved nutrients and oxygen in model studies (e.g. Anderson and Sarmiento, 1994; Schaffer, 1996; Schaffer et al., 1999) suggest ratios more in conformity to the globally averaged values reported by Redfield and colleagues than those reported for the particulate flux using sediment traps (Table 3). However, some uncertainty persists as to the changes in these remineralization ratios with depth; whereas Anderson and Sarmiento (1994), Takahashi et al. (1985) and Körtzinger et al. (2001b) find near-constant remineralization ratios with depth, Schaffer (1996) and Schaffer et al. (1999) estimate significant fractionation during remineralization of sinking organic matter in the upper 1500 m of the water column, with nutrients being released faster (i.e. shallower) than inorganic carbon. If the efficiency of the biological pump is defined as the amount of carbon per mole of limiting nutrient exported to below the depth of maximal mixing, this efficiency will depend on the C:N:P ratio of material exported from the euphotic zone as well as the relative remineralization of carbon and nutrients between the base of the euphotic zone and the depth of maximal annual mixing. The elemental stoichiometry of sinking particles is thus an important variable in the biogenic CO_2 flux between the ocean

and atmosphere. A preferential remineralization of nutrients to carbon in the mesopelagic zone would thus imply an efficiency of biological carbon drawdown in excess of that assumed using the Redfield ratios. If, by accounting for solubilization losses from sinking particles caught in sediment traps, the changing elemental composition of the sinking flux can be estimated, traps may provide reliable estimates of mesopelagic particle stoichiometry and remineralization ratios. Additionally, by providing material to characterize the composition and drivers of flux they are capable of yielding a more mechanistic understanding of upper ocean processes that effect the efficiency of the biological pump than large-scale nutrient fields can be expected to provide.

For calcite, losses from the particles are low and relatively constant. Lower solubilization of this inorganic carbon as compared to the high DOC_{ex} concentrations alters the Corg:Cinorg ratio (rain ratio) of flux at the base of the winter mixed layer (Table 2), that is responsible for net drawdown of atmospheric CO_2 by the biological pump. Net carbon (sequestration) fluxes at the winter mixed layer at the OMEX site as defined and calculated by Antia et al. (2001) increase by 50% (from 1.47 to 2.22 $\text{mgC m}^{-2} \text{yr}^{-1}$) in response to the increase in the rain ratio from 2 to 7 at 600 m depth when accounting for the particle-associated dissolved fluxes (Table 2). Integrated over basin-wide or global scales, this methodological caveat is significant.

Phosphorus fluxes are seldom reported in sediment trap studies, and indeed the extremely high C:P and N:P ratios found in the particulate fraction only (Table 1) are difficult to interpret. Even accounting for the more rapid remineralisation and loss of phosphorus from sinking particles compared to carbon and nitrogen, mid-water phosphate values present a constraint to loss rates that are far below those implied by N:P ratios of over 50:1 at the base of the mixed layer (Table 2). At the OMEX sites revising the elemental export values to account for particle solubilization brings the values in agreement with mid-water N:P and N:Si ratios of 16:1 and 3:1, respectively (calculated from the Levitus data set). The ability to measure the N:P and C:P ratios of export is useful especially in regions where nitrogen is in chronic under-supply to the euphotic zone, and in coastal regions where phosphorus can limit phytoplankton growth. The commonly assumed excess carbon over nitrogen and nitrogen over phosphorus in winter mixed layer export reported from sediment traps may largely be an artifact of the measurements though more data are needed to confirm this conclusion from other sites.

Biogeochemical studies investigating the efficiency of the biological pump in atmospheric CO_2 sequestration concentrate on the export of carbon to the limiting nutrient in excess of the Redfield value since this would supposedly enhance the oceans' role in the current climate debate. Should much of the "excess" fixed carbon be labile and respired near the surface, as is believed for the carbon-rich polysaccharide exudates of phytoplankton (Passow, 2002) this will have little

effect on net carbon export. Possible sites of over-Redfield carbon export to below the mixed layer are thus most likely in the upwelling and high-productivity regions of the tropical ocean, where annual mixing is shallow and highest net sequestration fluxes are found (Antia et al., 2001). If sediment traps can be used to more reliably estimate the stoichiometry of export, a range of other analyses in the sedimenting particles they collect could give valuable insight into the biological control of export and regional deviations from the global mean. This warrants attention in further studies.

5 Conclusions

- Elevated concentrations of dissolved elements in sediment trap supernatant points to losses from the sinking particles caught and introduces errors in the total flux measurements if the particulate fraction only is measured. These errors are of the same order as those due to hydrodynamic biases in collection efficiency
- The effects of solubilization on measurements of total elemental fluxes range from negligible for particle-reactive elements such as thorium and iron to substantial for rapidly recycled nutrients such as phosphorus
- For the major nutrients the degree of solubilization decreases in the order phosphorus, nitrogen, silica and carbon, and decreases with increasing water depth
- Element-specific differences in degree of solubilization results in errors in estimating the stoichiometry of export when the dissolved fraction is not measured
- Correcting for solubilization of the major nutrients results in revision of the C: N:P ratio of export from strongly phosphorus and slightly nitrogen-poor for the particulate fraction only to conform to the globally valid "Redfield Ratios" for the total (dissolved and particulate) fraction. This brings trap estimates in agreement with mid-water nutrient budgets and estimates of remineralisation along pycnoclines. The Rain Ratio (organic:inorganic carbon ratio) is also seen to be 4-fold higher at the base of the winter mixed layer when solubilization is corrected for.

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